

Supercritical Carbon Dioxide in Reactive Polymer Processing using Model Substrates

**By Erma Shah
S2921693**

Supervisors: Francesco Picchioni, Klaas Remerie

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Foreword

Contents of this report may overlap with the report produced by Emma Szoboszlai as the section “Supercritical Carbon Dioxide” in the introduction as well as parts of the methods and material section were written in collaboration with permission granted from our supervisor: Francesco Picchioni.

Abstract

Using supercritical carbon dioxide (scCO₂) as a solvent is a topic of immense interest in the reactive polymer-processing field. It is a non-toxic, inert, abundant and cheap resource, which can be exploited. This report encompasses a preliminary study of the effects on branching/degradation efficiencies of using scCO₂ as a solvent. The reaction is carried out between the organic peroxide Perkadox-PM (bis (4-methylbenzoyl) peroxide) and two model substrates for polyethylene and polypropylene, n-pentadecane and squalane respectively. The effect of varying temperature on peroxide efficiency was also studied. N-pentadecane showed branching efficiencies with a range of 27.35-37.15% in a temperature range of 110-150°C. The results demonstrated that increasing temperature increased branching efficiency. They also indicate that an environment of scCO₂ enhances branching efficiency. Squalane, on the other hand, exhibited degradation. Unfortunately, the product could not be observed or quantified by gas chromatography or ¹H-NMR. As a result, the experiment was repeated with measuring mass. A net mass loss was observed indicating that the degraded products escaped the system during depressurization.

Introduction

The macromolecular characteristics of polymers can greatly be enhanced by several different processing techniques. Polypropylene and polyethylene, two of the most commonly used polymers in industry, are upgraded by organic peroxides in two different manners. Polyethylene is subjected to crosslinking to enhance properties such as impact strength, abrasion resistance and environmental stress crack resistance [1]. In this form of upgrading, polyethylene chains join to form a dense network of three-dimensional polymer structure. Polypropylene, on the other hand, undergoes a controlled degradation of its backbone structure known as chain scission. The process lowers the molecular weight and the polymer melt viscosity, resulting in the polymer being less prone to shrinkage and warpage [2]. The industrial significance of organic peroxides is especially important because of these processes. Companies such as AkzoNobel are interested in such processes involving organic peroxides and upgrading of these processes is always an ongoing area of research. Recent developments suggest the potential of using supercritical carbon dioxide (scCO₂) as a solvent for reactive processing of polymers.

Supercritical Carbon Dioxide

In many cases, the processing of high molecular weight polymers involves polymer melts with high viscosities, which complicates their processing as high viscosity reduces material flow and increases heat generation and energy consumption [3]. Increasing the temperature can help overcome this issue however, the problem of polymer degradation arises at elevated temperatures. Considering such aspects, supercritical fluids, are of great importance for the processing of polymer melts of high viscosities, especially because of their plasticization effects, which allows the low temperature processing of polymers while avoiding degradation [4]. Supercritical fluids are also of interest due to their ability to facilitate the extraction of impurities from polymers, as well as polymer impregnation and process intensification.

Supercritical fluids, substances at pressures and temperatures above their critical values, are of great interest in the laboratory and in industry for polymer synthesis and processing applications. Specifically, supercritical carbon dioxide (scCO₂) is becoming increasingly studied and is distinguished for a multitude of reasons. Firstly, it is non-toxic, inert, abundant, inexpensive, and non-flammable. Moreover, carbon dioxide (CO₂) has critical conditions ($T_c=304\text{K}$ and $P_c=7.38\text{MPa}$) that are easily accessible[5], and its properties can be easily controlled by altering the temperature, pressure and/or chemical composition; for example, scCO₂'s density changes in response to small adjustments of pressure [4]. Inspection of the phase diagram of scCO₂, as seen in Figure 1, helps show that scCO₂ has a wide range of operating pressures and temperatures.

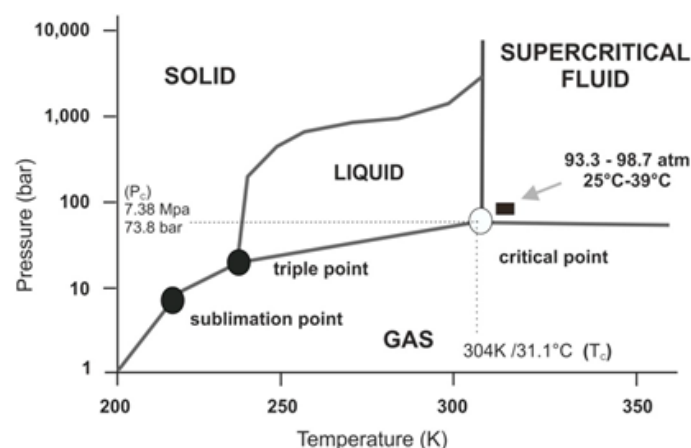


Figure 1- Phase Diagram of CO₂ [6]

Supercritical carbon dioxide's liquid-like densities and gaseous behavior make it a peculiar fluid, especially with regard to its use as a solvent. Above its supercritical temperature (304K), CO₂ cannot be liquefied by any pressure increase, thus the CO₂ exhibits gas-like viscosities, diffusivities and surface tensions [10]. Interestingly, scCO₂ can be compressed so that it is more dense than liquid CO₂

($\sim 0.47 \text{ g cm}^{-1}$) and can act as a solvent with lower viscosity than when it is in its liquid phase [7]. Further, its plasticization effect and ease of removal after a process by releasing the pressure contribute to its peculiarity.

The plasticization effect of scCO_2 can be explained by its properties. The low viscosity and surface tension of scCO_2 allow it to penetrate into polymer matrices easily [8]. Its dissolution in a polymer causes the plasticization of the polymer [4]; the supercritical fluid swells the polymer matrix inducing this effect. When this occurs, the glass-transition temperature (T_g) or melting point (T_m) of the polymer decreases, causing a decrease of viscosity. Therefore, the polymer is in a rubbery state at a much lower temperature, allowing the polymer to flow more easily as the polymer chains are more mobile [9]. By using scCO_2 , polymers can thus be processed at lower temperatures.

The extraction of impurities, impregnation with additives, and foaming can also be achieved. The use of scCO_2 to extract impurities is especially prevalent in the medical industry where polymer-based materials, including polyethylene, have direct contact with the human body. The ability of supercritical fluids to dissolve materials increases with increasing density, which can easily be controlled by manipulating the pressure and temperature. At ambient conditions, many materials are not soluble in CO_2 , however once it reaches its supercritical state, solute solubility can be increased up to ten times greater than those predicted by the ideal gas law [10]. On the other hand, impregnation of a polymer with additives is only possible when the solvent, or carrier liquid, can be dissolved in the supercritical fluid; the polymer is then exposed to the supercritical fluid mixed with the solute. Both miscible and immiscible substances can be dispersed into the polymer in this way [11]. Another use of supercritical fluids is in extruders to produce insulation foams on the industrial level. For example, MuCell Extrusion Technology [12] uses supercritical fluids in extruders to create microcellular foams.

The mention of multiple processes that utilize supercritical fluids introduces a significant engineering advantage: the compatibility of supercritical fluids with process intensification. A method for process intensification is to combine multiple steps of a process by the use of a single operation [13], such as the integration of polymer synthesis and foaming [9]. Another example of process intensification is using scCO_2 to remove impurities and facilitate polymer processing (e.g. plasticization). This can reduce capital costs as both processes can be carried out in one reaction vessel.

Although there are many advantages of using scCO_2 as a solvent in reactive polymer processing, several drawbacks exist that hinder its implementation on an industrial scale [14]. Introducing scCO_2 as a solvent requires relatively high-pressure equipment [29]; compressors can achieve these operating conditions however, implementing them involves high-energy consumption and thus significantly increases the operational costs. Relatively specialized equipment is also required in order to accommodate scCO_2 [30]. In light of this, scCO_2 would only be used for products that require the supercritical fluid and could otherwise not be manufactured. Further, scCO_2 , with its high quadrupole moment, is generally not a good solvent for hydrocarbons, and is reactive with good nucleophiles like amines, rendering it unfit as a solvent [29]. Additionally, its compatibility with industrial equipment is limited. For example, injection molding faces challenges regarding process economics and repeatability [31]. In processes such as gas-assisted injection molding, nozzle design is especially challenging as some nozzle designs can lead to fouling or plugging during injection or venting [32]. Lastly, carbon dioxide is a greenhouse gas and, despite emissions in large quantities, many regulations exist to ensure that limited amounts of carbon dioxide are released into the environment.

Reactions with Organic Peroxides

Nonetheless, the several advantages that scCO_2 provides has not got unnoticed and further research is being carried out to discover ways of implementing it in reactive polymer processing. Reactive polymer processing can be carried out with organic peroxides. These are classified as compounds that possess two oxygen atoms linked together with a covalent bond [16], also known as a peroxy group. The electronic and molecular structure of organic peroxides result in a weak -O-O- bond. Thereby, organic peroxides by nature are unstable molecules that undergo self-accelerating decomposition. Consequently, these compounds are exceptionally reactive and have great oxidative capabilities [17]. Organic peroxides can be used to process several polymers but the two processes that are the focus of this research are cross-linking and degradation in two of the most commonly used polymers in industry [15] polyethylene and polypropylene.

The initiation of both reaction occurs in a similar fashion. An organic peroxide decomposes by homolytic cleavage to form two radicals. The decomposition of Perkadox-PM (bis (4-methylbenzoyl) peroxide) is shown in Figure 2. The toluic radicals formed can undergo further rearrangement to form a toluene radical, liberating a CO₂ molecule as shown in Figure 3. Both radicals act as initiators and proceed to abstract a hydrogen atom from the polymer backbone.

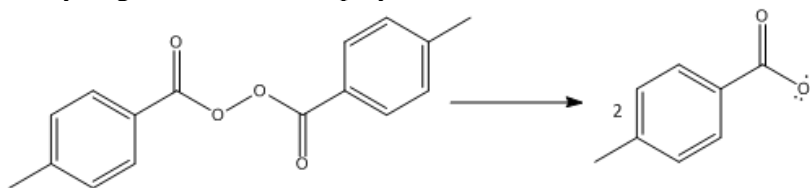


Figure 2 – Homolytic cleavage of Perkadox-PM to form two toluic acid radicals

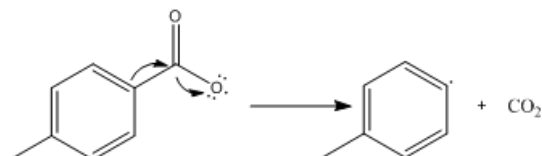


Figure 3– Formation of toluene radical and carbon dioxide

In chain scission, a hydrogen is abstracted from a polymer backbone to form a polymer radical as shown in Figure 4. Chain scission continues by a macro radical rearrangement, known as an elimination reaction, forming a lower molecular weight polymer as depicted in Figure 5. [32]

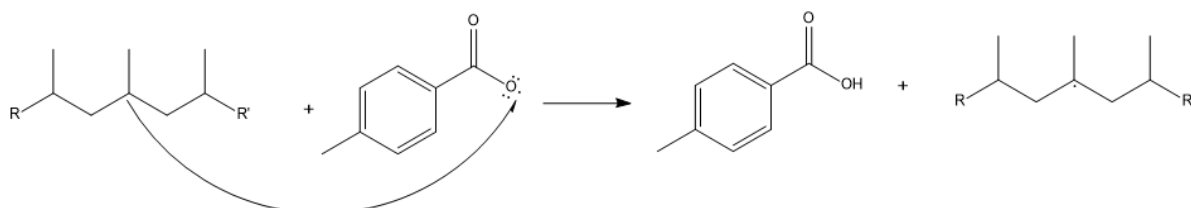


Figure 4– Abstraction of hydrogen from polypropylene backbone to form toluic acid and a polymer radical

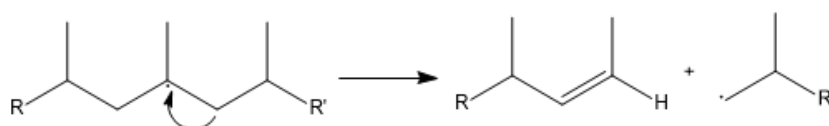


Figure 5– Unsaturation of polymer

Cross-linking is initiated with the same decomposition of peroxide as shown in Figures 2 and 3. It continues also with a hydrogen abstraction resulting in a polymer radical as depicted in Figure 6. Termination of the cross-linking reaction occurs when two polymer radicals combine to form a branched polymer as shown in Figure 7.

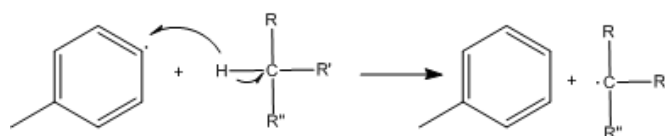


Figure 6– Hydrogen abstraction and formation of polymer radical

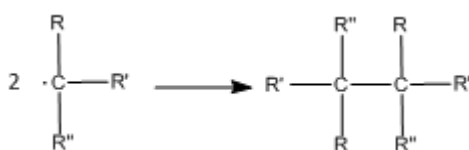


Figure 7– Branching of polymer

Polymers can undergo either branching or elimination reactions (Appendix A). Both reactions have different activation energies and as a result, the reaction pathway that a polymer takes is determined by kinetics. Figure 8 gives a visual representation of how temperature effects the speed of a reaction. This plot is determined by the Arrhenius equation shown in equation (1) (where k is the rate constant, E_a is the activation energy, R is the gas constant, T is temperature and A is the pre-exponential factor). Figure 8 shows that at a higher temperatures, the speed at which elimination reaction occurs is much greater than speed at which a branching reaction occurs [27]. For this reason, at higher processing temperatures the elimination reaction is favored, whereas branching is favored at lower processing temperatures. This can also be explained by considering the mobility of the polymer chains. At lower temperatures, the polymer melt experiences higher viscosities, which leads to a lower mobility of the macro radicals formed. At higher temperatures, there is greater mobility in the macro radicals and so there is a greater chance for a macro radical rearrangement, which favors chain scission [18]. Temperature is not the only factor that determines what reaction takes place. Other factors that may affect reaction pathways include molar mass, shape of molar mass distribution and branching levels [19].

The point of intersection in the Arrhenius plot plays an important role in selecting the temperature for polymer processing as it determines which reaction pathway the polymer will take. For polyethylene, the point of intersection occurs at around 300°C whereas for polypropylene it is around 100°C [27]. If processing of polymers occurs at temperatures below the point of intersection, branching reactions are predominant and conversely, if processing occurs at temperatures above the point of intersection, elimination reactions are predominant.

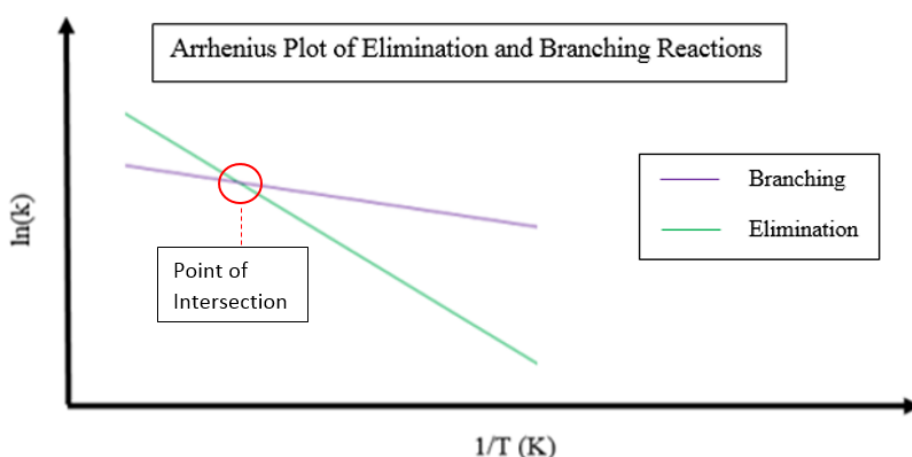


Figure 8- Speed of branching and elimination reactions as a function of temperature. The lines represent arbitrary values

$$(1) \ln(k) = \frac{-E_a}{RT} * \frac{1}{T} + \ln(A)$$

In this research, n-pentadecane was used as a model substrate for polyethylene and squalane was used as a model substrate for polypropylene (structures shown in Figure 9). Both hydrocarbons were reacted with the organic peroxide Perkadox-PM. The liberation of toluene makes Perkadox-PM an unfavorable peroxide in applications on an industrial scale. Risk factors, peroxide compatibility, as well as the kinetic data of the organic peroxide are taken into account when selecting the appropriate peroxide. Di-tert-butyl peroxide is one of the preferred peroxides as it liberate a relatively safer compound during decomposition and is one of the more stable peroxides [28]. Thus, Perkadox-PM is also a model substrate for an organic peroxide that would be used in industry for polymer modification.

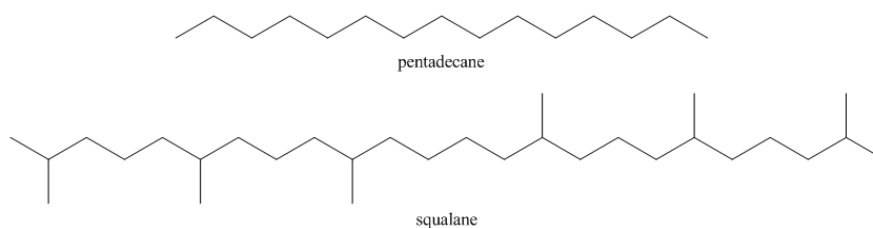


Figure 9– Starting materials *n*-pentadecane (above) and squalane (below)

The reaction will also use scCO₂ as the solvent. In order to have CO₂ in its supercritical state, a pressure up to 100-120 bar was inserted. A study conducted on the effect of high pressure on cross-linking of polyethylene concluded that radical initiators decompose at a slower rate with increasing pressure [20]. In the case for both reactions, this would result in lower peroxide efficiency as the production of primary peroxide radicals would decrease. However, the pressures used for this study were far greater than 80 bar, ranging from 3000 to 8000 bar. Therefore, the stabilization effect of pressure on the peroxide radicals will most likely be negligible.

Ideally, the only product that should form during the branching reaction in *n*-pentadecane is the *n*-pentadecane dimer shown in Figure 10a. However, multiple hydrogens may be extracted from the same hydrocarbon backbone. This would result in the formation of the product shown in Figure 10b. This would especially be prevalent if miscibility between Perkadox-PM and *n*-pentadecane is poor. Moreover, although unlikely, trimers or tetramers may form if the peroxide is highly reactive or in too high concentrations. A tetramer of *n*-pentadecane is shown in Figure 10c. Additionally the formation of toluic acid could also interfere in the reaction. If this is the case, a moiety such as that shown in Figure 10d may form. If oxygen were present in the system, it too would interfere in the reaction and provide different versions of cross-linked pentadecane dimer. Examples of products that may form with oxygen are shown in Figure 10e and 10f.

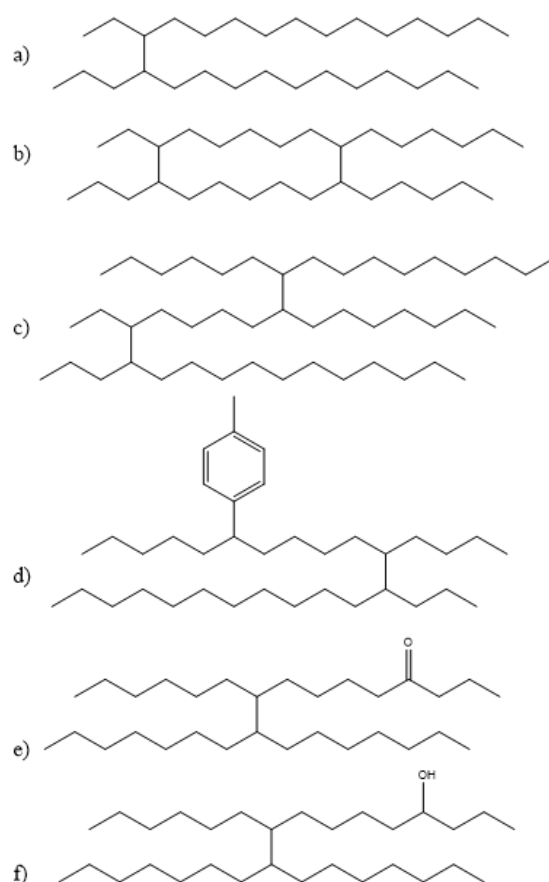


Figure 10 – Different variations of branched products that may form during branching reaction of *n*-pentadecane

Products in the elimination reaction of squalane can also take various forms. Depending on where the hydrogen is abstracted, products can have a carbon number up to C-29. Figure 11 shows some of the structures of the degraded products that may form. Figure 12 a, b and c depict a product having carbon numbers of C19, C15 and C10 respectively.

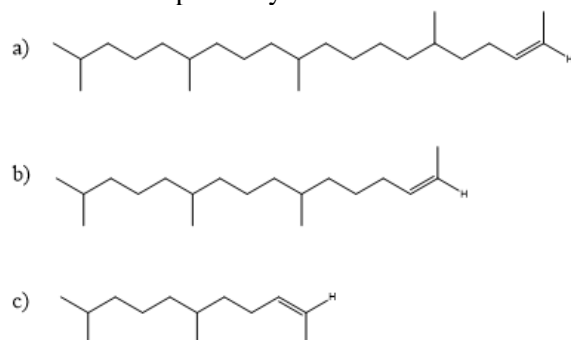


Figure 11- Potential degraded products of Squalane

Research Question and Hypotheses

The goal of this research was to test peroxide efficiency in an environment with and without $scCO_2$. Additionally, the effect of temperature was taken into account. Thus, the research question is sub categorized into two questions. In a reaction carried out between n-pentadecane/squalane and Perkadox-PM: how does peroxide efficiency compare in an environment with and without supercritical carbon dioxide? What role does temperature play in this reaction?

Three sets of experiments were carried out to facilitate this research. The first experiment tested solubility of each hydrocarbon in $scCO_2$. This was required in order to determine the correct concentration of peroxide in the system. Additionally, it provided insight on compatibility between the hydrocarbon and the $scCO_2$ atmosphere.

Higher molecular weight compounds have stronger van der Waal's dispersion forces, which hinders dissolution of n-pentadecane in $scCO_2$. A study concluded that aliphatic hydrocarbons with a carbon number greater than C12 show a rapid decrease in solubility with increasing carbon number [21]. Therefore, it was expected that squalane, having a carbon number of C30, should be nearly immiscible however, n-pentadecane, having a carbon number of C15, might show partial solubility.

The next set of experiments tested the effect of temperature, ranging from 110-150°C, on the peroxide efficiency of n-pentadecane in $scCO_2$ using Perkadox-PM. N-pentadecane was used as a model substrate for polyethylene. Therefore, it was expected that n-pentadecane would mimic the branching reaction of polyethylene. A study carried out by AkzoNobel reacted benzoyl peroxide with n-pentadecane at 137°C and no solvent. The results portrayed a branching efficiency of 27% [22]. Although the study used a slightly different peroxide and different equipment, the results were used as a rough approximation for what to expect in the n-pentadecane experiments.

Lastly, the same experiment was carried out with squalane. Squalane represents polypropylene. Therefore, it is expected that squalane should also undergo an elimination reaction and produce degraded products. Peroxide concentration plays an important role in the type of product that is degraded. A peroxide concentration greater than 0.3 w.t.% is considered quite high [23]. In this experiment, a 4.47 w.t.% peroxide concentration was used. Therefore, products with a lower carbon number are expected.

The effect of temperature on the efficiency of the n-pentadecane and squalane experiments was expected to be the same. The amount of decomposed peroxide was kept at a constant value of at least 99% (for calculations go to Appendix B). Thus, the same amount of radicals were liberated at each experiment. However, at a higher temperature, the rate at which the peroxide decomposes is faster, which results in an increase of instantaneous radical concentration. This effect promotes branching/degradation in the polymer. A higher temperature may also have an effect on solubility. If increasing temperature results in an increase in peroxide solubility in the hydrocarbon, it would result in greater contact between the two reactants and hence increasing temperature would increase efficiency.

Materials and Methods

Materials

Perkadox-PM-W75 was kindly supplied by AkzoNobel (The Netherlands) with an assay of approximately 75% on water. N-Pentadecane (>99% volume) and squalane (>99% volume) were purchased from Acros Organics.

Solubility of N-pentadecane and Squalane in scCO₂

2.5 mL of respective hydrocarbon was inserted in a 65mL view-cell autoclave equipped with a mechanical stirrer at room temperature and ambient pressure. After sealing, the vessel was flushed with CO₂ for approximately 10 seconds. The vessel was then heated to a temperature of 110°C, which took approximately 15 minutes. Once the desired temperature was obtained, the pressure was increased to 80 bar. Then the stirrer was switched on at 1000 RPM and the hydrocarbons were observed for any visible changes.

Reactor Setup

A double walled stirred reactor (100mL) was used for the pentadecane and squalane experiments. It was equipped with an electric heating element with a temperature controller, and a high-pressure pump unit with CO₂ and N₂ tanks. The reactor, which is equipped with a mechanical stirrer and Rushton type impeller, can reach a maximum temperature of 250°C and a maximum pressure of 10 MPa. A membrane pump (Lewa) with a capacity of 60 kg/h at a maximum pressure of 35 MPa comprises the high-pressure pump setup. Prior to being fed to the pump, the CO₂ is cooled to 0°C by a heat exchanger. After the pump, a heat exchanger is used to heat the CO₂ to the necessary temperature. A diagram of the high-pressure reactor setup is shown in Figure 12.

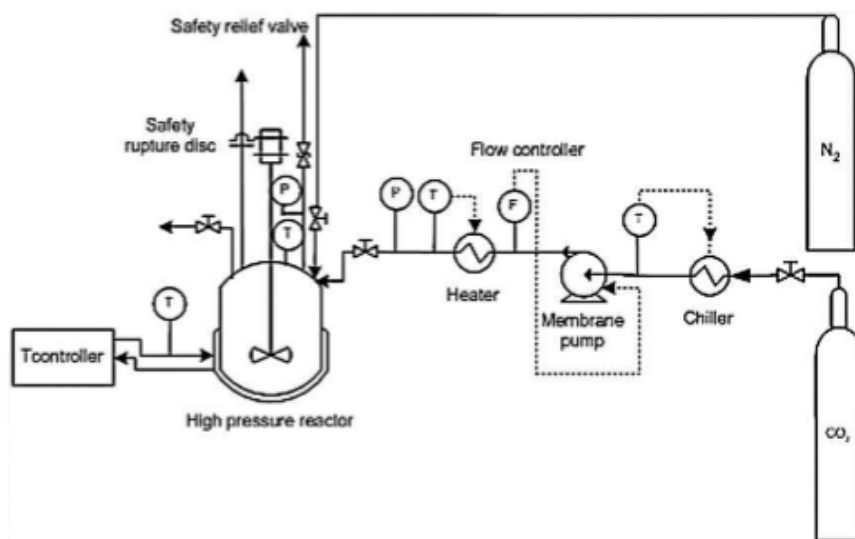


Figure 12 – Schematic diagram of reactor set-up [24]

Experimental Procedure for the Reaction of N-Pentadecane/Squalane with Perkadox-PM

Perkadox-PM (0.3610g, 0.1 M, 0.001mol, 75 w.t.% on water) and the hydrocarbon (10mL) were added to the reactor. The vessel was flushed with CO₂ at ambient pressure for roughly 15 seconds and then sealed from the environment. The reactor was pressurized to 20 bar with CO₂, and the desired reaction temperature was set. The mixture was stirred at 1000 RPM, with the Ruhstom blade submerged in the hydrocarbon. Once the temperature in the autoclave reached a value within 20°C of the desired

temperature, the reactor was further pressurized with CO₂ to 80 bar. After the desired reaction temperature was reached, the reaction was left for a suitable time depending on the reaction temperature. The time for each reaction was determined by calculating how long it would take the peroxide to undergo ten half-lives at that temperature. Calculations can be found Appendix B. The reaction times and their corresponding reaction temperatures are shown in Table 1. Additionally, after the reaction time was reached, the heating element was powered-off and cooling water was used to cool the reactor. After a temperature of 40°C was reached, the CO₂ was slowly released to depressurize the system to atmospheric pressure. Each experiment for every temperature was repeated three times. Additionally, the same reaction was carried out at 130°C without scCO₂. This was done by flushing the air out of the system with nitrogen.

Table 1: Reaction temperatures and corresponding reaction times

Reaction Temperature (°C)	Reaction Time (minutes)
110	30
130	5
150	1

Analytical Equipment

All samples were measured with Gas Chromatography with Flame Ionization Detection (GC-FID). A GC-FID (Agilent Technologies, 7890B, GC System) apparatus was used to identify the concentration of product in each sample. The FID detector operated at 300°C and the injector temperature was at 280°C with a volume of one µL. The split ratio was 1:50 and the column had a flow of 1 mL/min. The oven temperature program was set to 40°C -0 min - 5°C /min - 250°C -3min.

In order to perform these analyses, samples were created with a 1:1 solvent, tetrahydrofuran (THF), and sample ratio. Five calibration samples of squalane were prepared with varying concentrations of: 2463 ppm, 1806 ppm, 1231 ppm, 612 ppm and 246 ppm. Additionally, some samples were compared against the National Institute of Science and Technology (NIST) library for identification purposes.

Results and Discussion

The raw data as well as the processed data, along with all calculations, for the experiments can be found in Appendices C and D. Refer to the corresponding Appendix when necessary.

Solubility of N-Pentadecane and Squalane in scCO₂

Both hydrocarbons appeared as clear liquids. However, squalane was more viscous than n-pentadecane. After pressurizing, a swelling effect was visible in both hydrocarbons. It was especially noticeable in the squalane sample. The experiment indicated that neither n-pentadecane nor squalane were soluble in scCO₂ as two separate phases were clearly visible in the reactor. Figure 13 depicts the results of the experiment. The lower phase belongs to the respective hydrocarbon and the upper phase belongs to scCO₂. The red arrow shows the two separate phases.



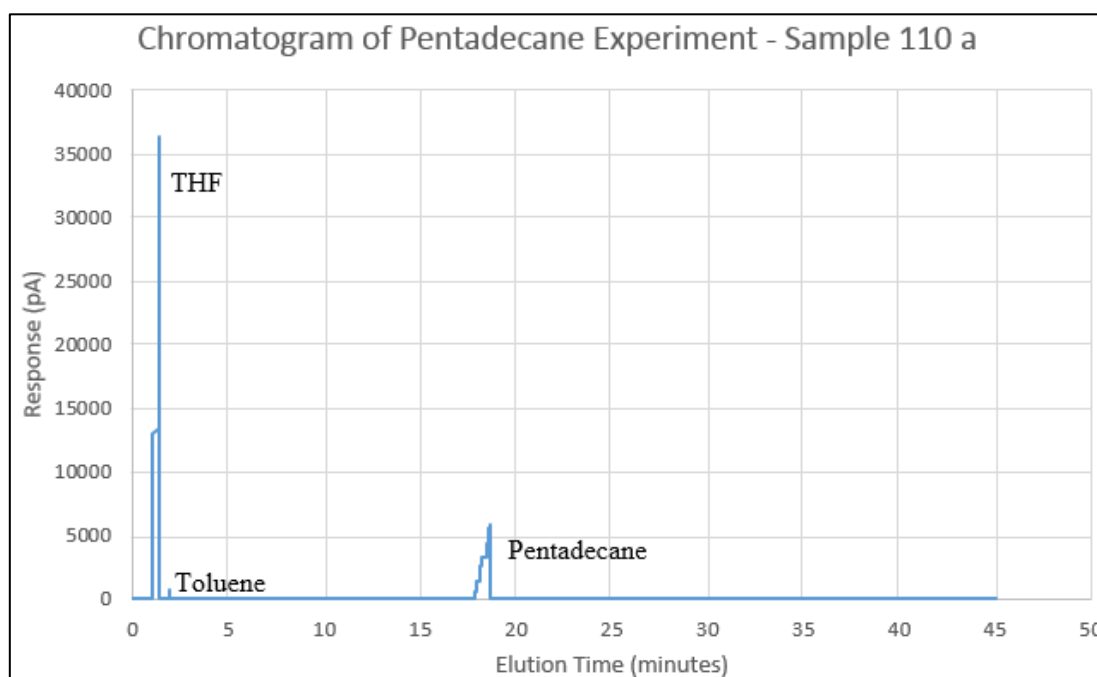
Figure 13 – Results of solubility experiment on *n*-pentadecane (left) and *n*-squalane (right) in *scCO*₂

The analysis for this experiment was only performed qualitatively, which means that partial solubility of hydrocarbon in *scCO*₂ cannot be ruled out as an option. However, in order to determine the concentration of peroxide in the system, it was assumed that both hydrocarbons, *n*-pentadecane and squalane, were immiscible.

Effect of scCO₂ and temperature on n-pentadecane reaction with Perkadox-PM

N-pentadecane appeared as a clear liquid. During the experiment, after pressurizing the system, a further pressure increase was observed to approximately 100 bar. The pressure increase could be a result of the formation of carbon dioxide or other volatile compounds. The final product was mostly a clear liquid, similar to *n*-pentadecane, however, a white precipitate was observed for every reaction sample. This white precipitate may indicate the presence of a trimer or a tetramer or it could also be toluic acid which also takes the form of a white powder [34]. Additionally, bubbles were observed rising to the surface in the product sample when it was freshly extracted. These bubbles most likely belonged to CO₂. The formation of bubbles stopped after a few minutes.

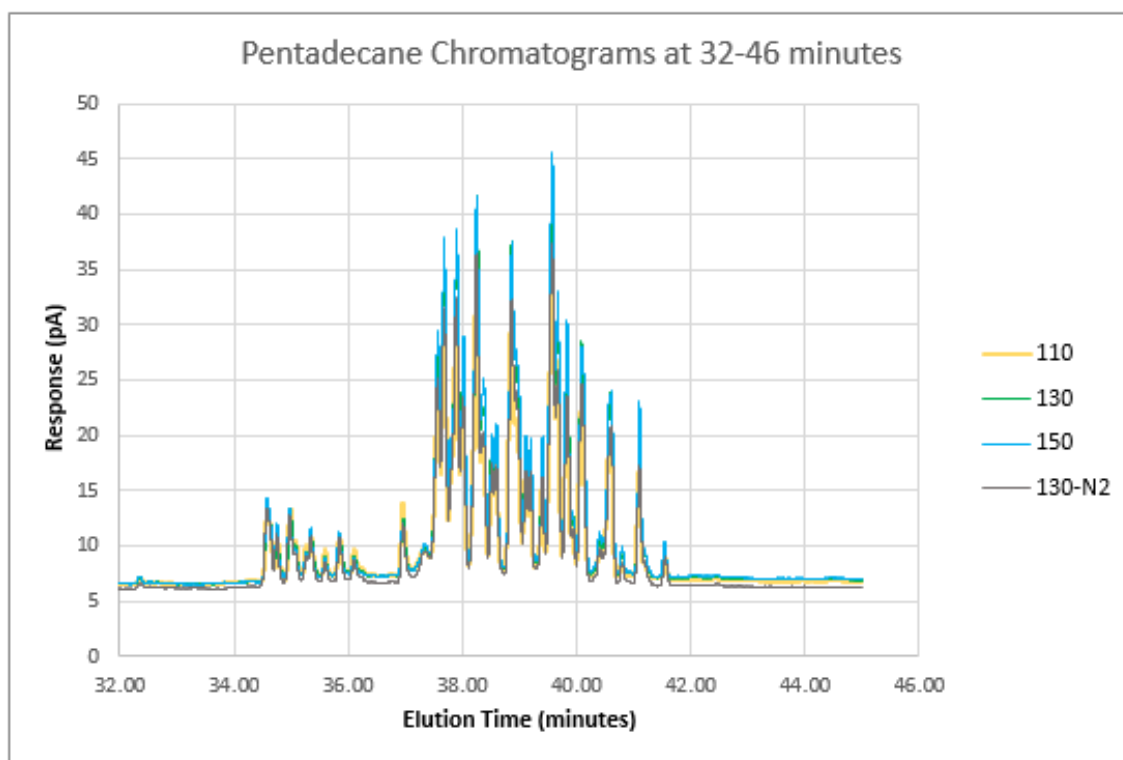
The chromatogram obtained from GC-FID for one of the *n*-pentadecane experiments (110 a) is shown in Graph 1. All of the samples had chromatograms similar to the one shown in Graph 1. There are three visible peaks: one for the solvent THF at about 1.5 minutes, one for the by-product toluene at about 2 minutes and one for the reactant *n*-pentadecane at about 18 minutes. The dimer product is not visible in the chromatogram.



Graph 1 – Chromatogram of *n*-pentadecane experiment sample 110 a

Enhancing the chromatogram showed several peaks. These peaks belonged to the dimer product as well as by-products that came from the peroxide. To identify the peroxide peaks, Perkadox-PM was reacted with THF at the same conditions and the product was tested with GC-FID. Many peaks were visible in the elution time range of 12-22 minutes. Therefore, it was deduced that any peaks in that time region belonged to the peroxide by-products.

In order to determine the elution time of an n-pentadecane dimer, an external standard of a pure n-pentadecane dimer was required. However, since that was not available, another hydrocarbon with a carbon number of C-30 was used: squalane. Although squalane has a different structure and molecular weight than a pentadecane dimer, it was used as an estimate for the elution time of an n-pentadecane dimer. Via the NIST library, it was deduced that an n-pentadecane dimer should elute at around 35 minutes at the given settings. A region between 32-42 minutes was chosen to account for the potential variations of dimers that may form which would lead to slightly different elution times. An enhanced version of the chromatogram at this period is shown in Graph 2. From Graph 2 it can be deduced that all the samples of the n-pentadecane experiment eluted the same product, which can be seen by the overlap of all peaks for the three different temperatures and the two different environments. Graph 2 also shows multiple peaks instead of a single one, which means that variations of dimer had formed, similar to those shown in Figure 10. The different intensities of the peaks indicate that all samples had different concentrations of product.



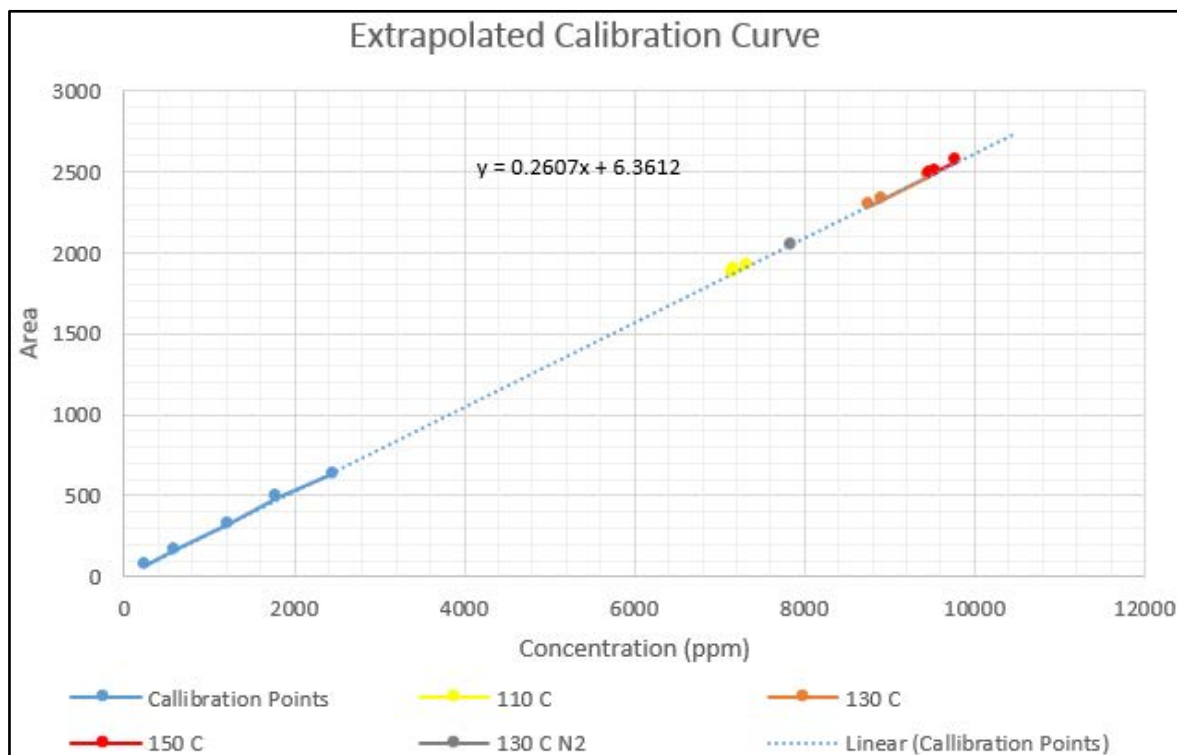
Graph 2 – Chromatogram for n-pentadecane experiment sample 110 a at minutes 32-46

In order to quantify the amount of product that had formed, calibration samples of n-pentadecane dimer was required. Since the n-pentadecane dimer was not available, squalane was used for the calibration samples as well. Because squalane was used instead of the n-pentadecane dimers, the results will only provide a rough estimate for the concentration of product and branching efficiency in the samples. For results that are more accurate n-pentadecane dimers must be used as an external standard.

The five calibration samples of squalane that were prepared had concentrations of 2463 ppm, 1806 ppm, 1231 ppm, 612 ppm and 246 ppm. After testing the samples with GC-FID, the area of the peaks obtained from their chromatogram was plotted with respect to their concentrations. A straight line was received with the equation shown in equation (2).

$$(2) y = 0.2607x + 6.3612$$

The line was extrapolated and the area obtained from the chromatograms at the elution time from 34 until 42 minutes was used to determine the concentration of dimer in the GC-FID samples. Graph 3 depicts the results. Graph 3 indicates that with increasing temperature the concentration of dimer products also increased. It also shows that using scCO₂ as a solvent provides a greater concentration of dimer product.



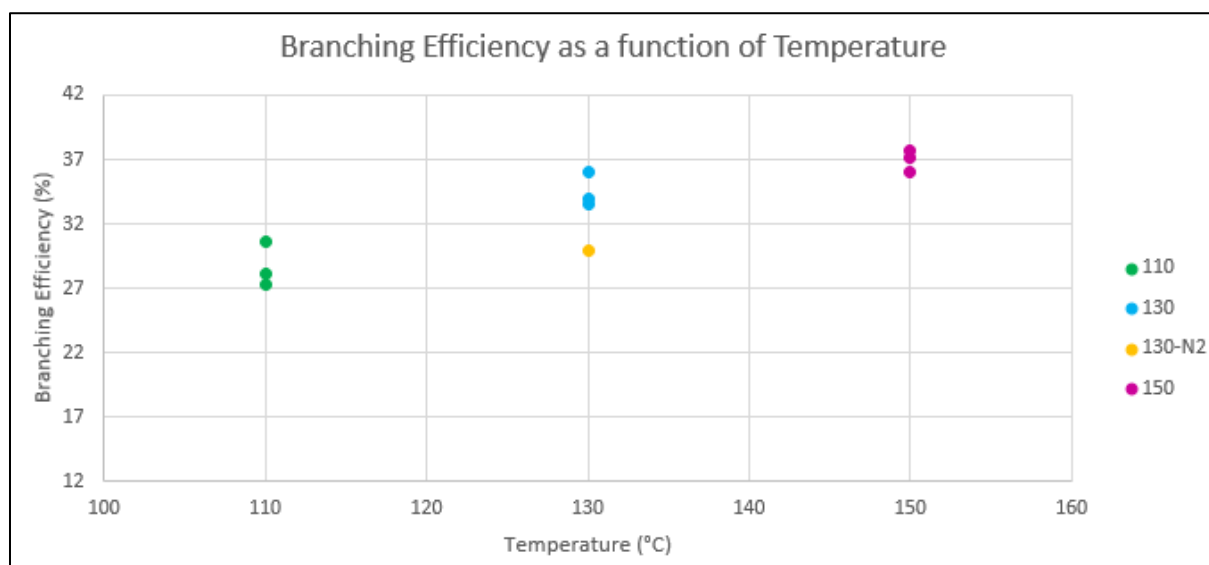
Graph 3 – Extrapolated calibration curve showing concentrations of various samples.

From the concentration of dimer product in the GC-FID samples, the concentration of dimer product in the reaction samples could be determined. From this information, the branching efficiency was calculated. Appendix D shows the calculations for the branching efficiencies of each sample. These calculations were based on the assumption that each dimer only has one cross-link. A branching efficiency range of 27.35-37.15% was calculated. The branching efficiency was plotted with temperature as shown in Graph 4. This graph shows that, similar to Graph 3, increasing the temperature increased branching efficiency and an environment of scCO₂ favored branching efficiency.

The experiment done under a nitrogen atmosphere mimicked a situation where no solvent was present. This sample had a branching efficiency of 29.92%, whereas the samples with scCO₂ as a solvent, at the same temperature, had an average branching efficiency of 34.48 ± 2.56 %. Although the difference is small, the results suggest that scCO₂ had an effect on the reactions. It indicates that n-pentadecane did indeed exhibit partial solubility. However only one sample under a nitrogen atmosphere was carried out due to limited quantity of n-pentadecane. This one sample may be an anomaly and therefore it is insufficient to reach a definitive conclusion. Nonetheless, a study conducted with benzoyl peroxide [25] also had a similar result.

Increased branching efficiency was also observed with increasing temperature. At ambient conditions Perkadox-PM was not soluble in pentadecane. However, it could be that increasing the temperature may have led to an increase in peroxide solubility. This would provide a more homogenous reaction environment. Increasing the temperature may also allow for greater swelling in the polymer, which in turn would increase diffusivity and would provide a better environment for the reaction to take place. The solubility of the peroxide in n-pentadecane under scCO₂ was not tested due to the lack of pentadecane. However, it may play an important role in understanding the role of temperature in this

reaction. Additionally, increasing temperature would increase the rate of radical formation thereby increasing the instantaneous radical concentration and therefore increasing the branching efficiency.



Graph 4 – Average branching efficiency with respect to temperature

Furthermore, because the branching efficiencies were in such a close proximity to one another and because only three samples were taken for each sample, a T-test was performed on each of the sets of data points [26]. If the two groups of data show a p value of less than 0.05, the data is considered statistically significant and the null hypothesis cannot be ignored. The results for the three groups of data are shown in Table 2.

Table 2: Results of T-test

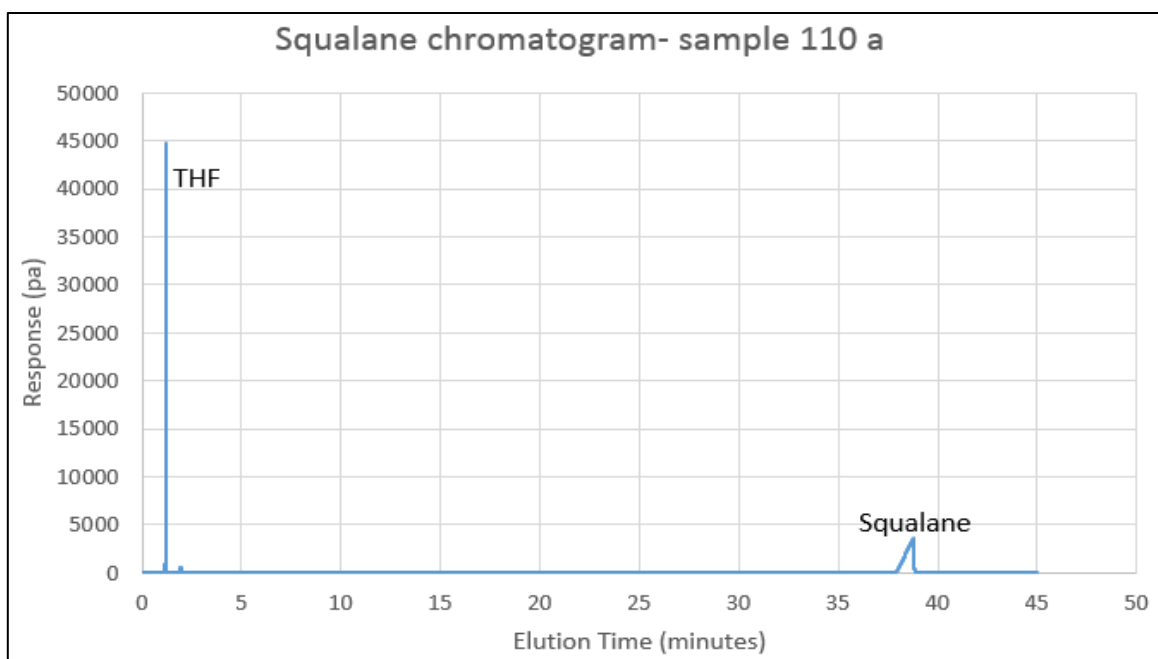
Groups	P value
110°C and 130°C	0.0101
130°C and 150°C	0.0549
110°C and 150°C	0.0017

The data points of the samples at 130°C and 150°C showed a p value which was greater than 0.05. The two other groups that were compared had a p value less than 0.05. This result suggests that there is a direct correlation between temperature and branching efficiency. However, it also suggests that increasing the temperature above a certain point, leads to very little increase of branching efficiency.

Effect of scCO₂ and temperature on squalane reaction with Perkadox-PM

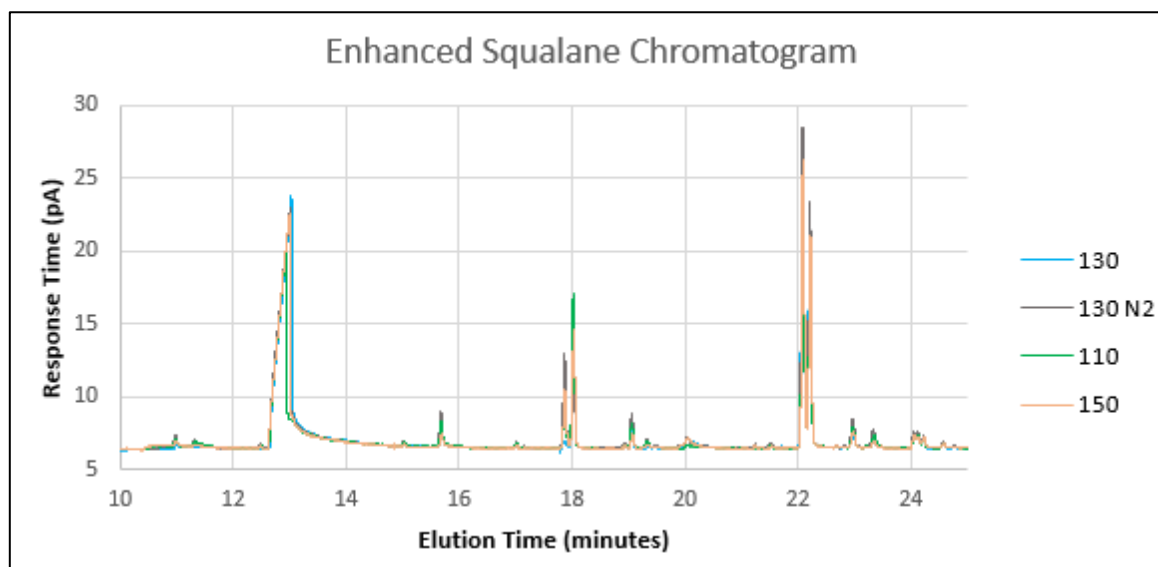
Squalane was a clear liquid, which was much more viscous than n-pentadecane. The experiments had a pressure increase of about 120 bar, indicating that a greater amount of volatile compounds had formed. A white precipitate in greater quantities was observed. Since squalane should degrade and not form branched products, it is more likely that the observed white precipitate is toluic acid.

After testing the samples with GC-FID, a chromatogram depicted in Graph 5 was observed for all samples. Two main peaks were observed. The first one belongs to THF at approximately 1 minute. Squalane is seen at about 37 minutes. The peak for toluene is almost not apparent but it is present at approximately 2 minutes.



Graph 5 – Chromatogram for squalane experiment sample 110 a

Several versions of degraded products of squalane should have been present. Therefore, it was assumed that the degraded products should have eluted between the times 12-25 minutes. The chromatogram was enhanced in this region in Graph 6 was observed.



Graph 6 – Enhanced squalane Chromatogram

The chromatogram showed that negligible amounts of degraded product. The few peaks that are observed belong to the by-products of Perkadox-PM. A blank sample for Perkadox-PM was prepared by reacting it with THF at 130°C. When this was measured in GC-FID, it too showed peaks similar to those shown in Graph 6. The reason for non-observable product could be that when squalane degraded, the carbon number of the degraded polymer reached below C12. When this happens, the polymer is soluble in scCO₂ and therefore it can escape the system during depressurization. This could also explain why the pressure reached 120 bar during the experiment.

The product sample was analyzed by $^1\text{H-NMR}$ spectroscopy as well. The $^1\text{H-NMR}$ spectra of the product can be found in Figure 14.

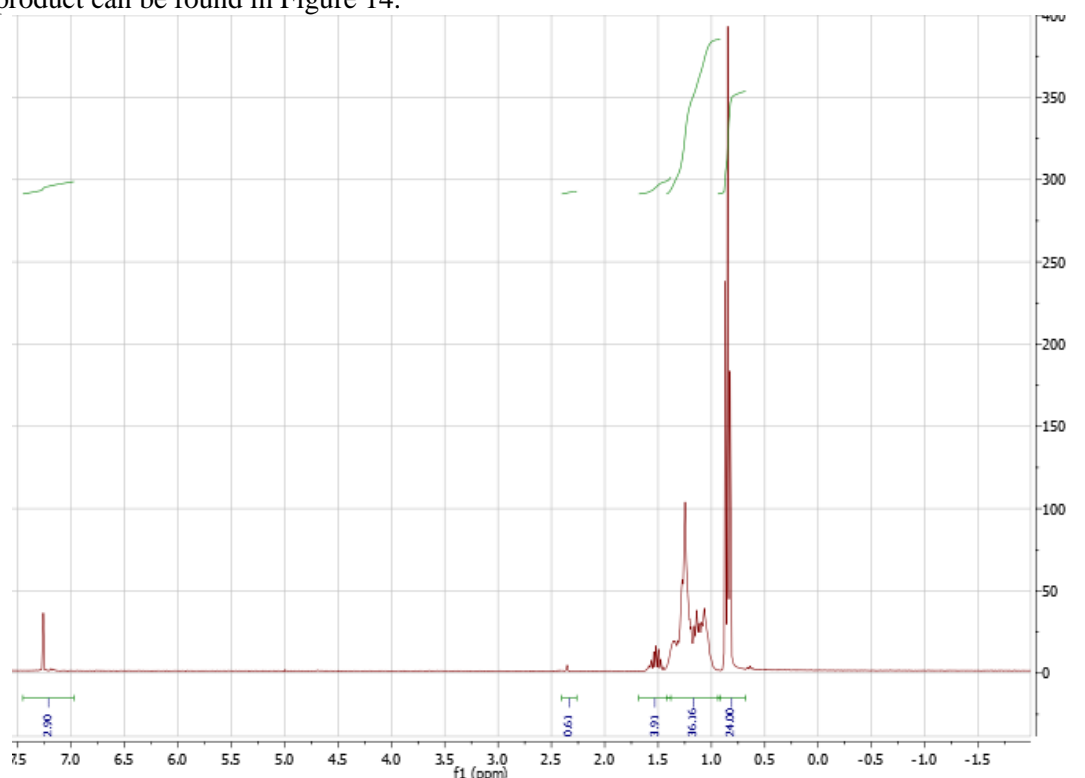


Figure 14 – $^1\text{H-NMR}$ spectra of product of squalane experiment sample 110 b

Figures 15 and 16 represent toluene and squalane with labeled carbon atoms. Table 3 shows which hydrogen are represented in the peaks in Figure 14. The $^1\text{H-NMR}$ results show that most of the product was squalane with very small amounts of toluene.

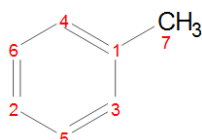


Figure 15 - Toluene with labeled carbon atoms

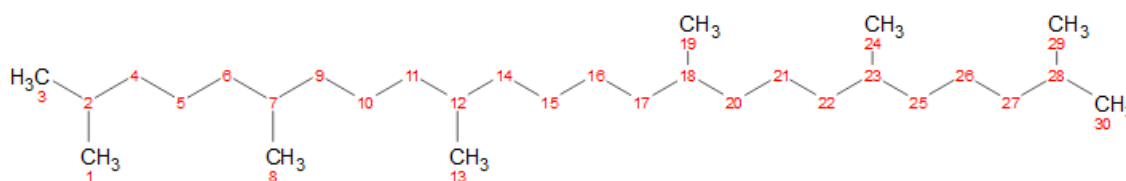


Figure 16- Squalane with labeled carbon atoms

Table 3 – $^1\text{H-NMR}$ interpretation

Peak	Type	Hydrogen corresponding to carbon number	
		Toluene	Squalane
0.75 ppm	Triplet	-	C1, C3, C8, C13, C19, C24, C29, C30
1-1.3 ppm	Multiplet	-	C4, C5, C5, C9, C10, C11, C14, C15, C16, C17, C20, C21, C22, C25, C26, C27
1.5 ppm	Multiplet		C2, C7, C12, C18, C23, C29
2.4 ppm	Singlet	C7	-
7.4 ppm	Multiplet	C1, C2, C3, C4, C5	-

Since neither analysis techniques showed that squalane exhibited degradation, to confirm that degradation took place and the degraded products left the system, another experiment was performed at 130°C with scCO₂ as the solvent. The weight of the contents were measured before and after to see if there was a difference. The details of the experiment can be found in Appendix E. In the end, there was a difference of 0.1853g. This difference does not necessarily have to be only of degraded product. It could also be the result of loss of carbon dioxide in the system. However, assuming that all the initiator radicals were toluic radicals, the mass lost is still more than the amount of carbon dioxide that is released by 0.0676 grams. This result indicates that indeed degradation took place and the degraded products escaped the system during depressurization.

Conclusion

The research encompasses a preliminary study of using scCO₂ as a solvent for crosslinking/degradation reactions between n-pentadecane/squalane and Perkadox-PM. Solubility experiments showed no visible sign of either hydrocarbon being soluble however, further results indicates presence of partial solubility. Experiments, of temperatures ranging from 110°C to 150°C, with n-pentadecane resulted in branching efficiencies ranging from 27.35-37.15% . Performing a T-test on the sets of data indicated that there was a correlation between temperature and efficiency. However, after a certain point, the increase in branching efficiency is not as significant. Moreover, the results indicate that using scCO₂ as a solvent achieves greater crosslinking efficiencies. This suggests that scCO₂ would be a suitable solvent for crosslinking of polyethylene; however, a further investigation using polyethylene is required to reach this conclusion as scCO₂ may have a different effect on polyethylene due to its increased molar mass. On an industrial scale, exploiting scCO₂ in reactive polymer promising may be an area of interest because of the considerable increase in branching efficiency that it provides. However, an economic analysis must be carried out to confirm if the increase in branching efficiency outweighs the cost of the high pressures required to achieve scCO₂.

The elimination reaction with squalane could not be quantified as negligible amounts of degraded polymer were detected with GC-FID and ¹H-NMR. The reason for the lack of detection was that hydrocarbons with carbon numbers smaller than C12 were being produced. Consequentially, the hydrocarbons were miscible in scCO₂ and escaped the system during depressurization. Repeating the experiment by measuring the weights resulted in a net loss of mass, which confirms that the degraded products indeed left the system during depressurization.

Using a hydrocarbon with a greater carbon number, would result in degraded product that is immiscible in scCO₂. If this is the case, the reaction can be quantified more effectively. Therefore, it is suggested to the repeat experiment with a different model substrate for polypropylene; one that can produce degraded hydrocarbons that are not miscible with scCO₂. Additionally, lowering the concentration of peroxide may also aid in producing degraded products that are not miscible in scCO₂.

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Appendix A: Reaction Overview

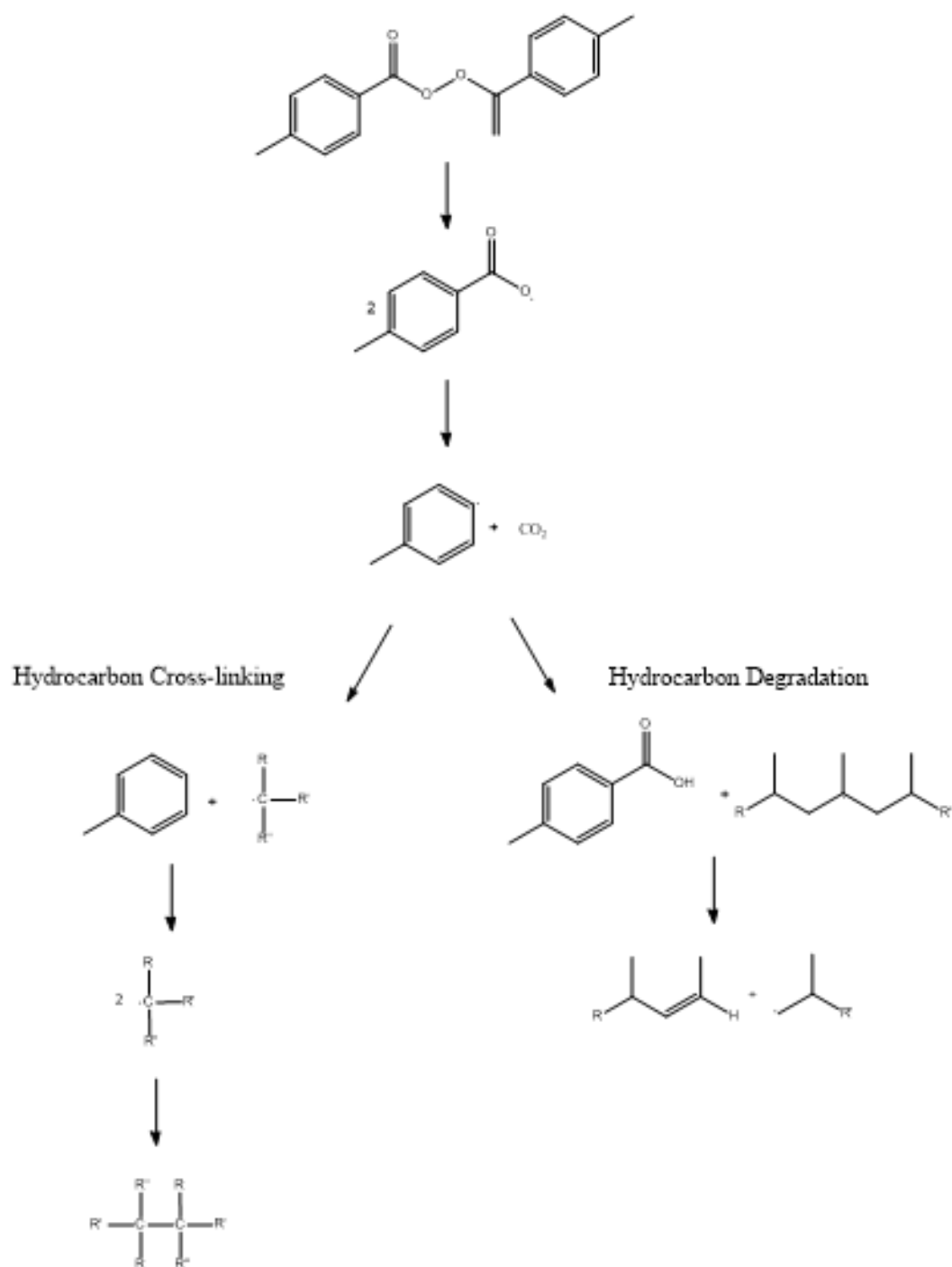


Figure 15 – Reaction pathways

It should be noted that the branching and elimination reactions take place with either initiator molecules: the toluene radical or the toluic acid radical.

Appendix B: Half-Life Calculations

The half-life was calculated using a series of two equations. The Arrhenius equation, shown in equation (2), was used to calculate the rate constant k . Once the rate constant was known, equation (3) was used to calculate the half-life, in seconds, for 99% decomposition. The values for the constants can be found in Table 4.

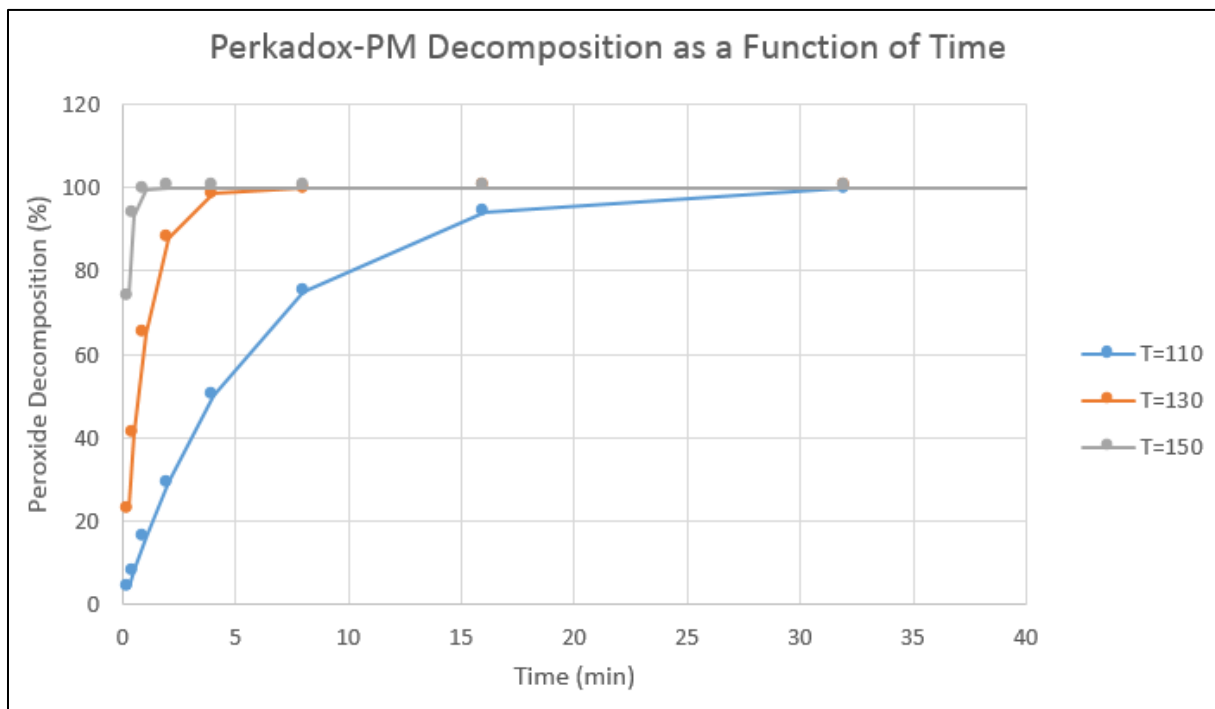
$$(1) k = Ae^{-\frac{E_a}{RT}}$$

$$(2) t = \frac{\ln \frac{100}{100-99}}{k}$$

Table 4: Constants of Perkadox- PM used for equations (2) and (3)

Gas Constant (J/kmol)	R	8.314
Arrhenius pre-factor	A	1.69×10^{13}
Activation Energy (J)	E_a	115,600

The results are plotted in Graph 7. They show that for 99% decomposition of Perkadox-PM, 30 minutes, 5 minutes and 1 minute are required for the temperatures 150°C, 130°C and 110°C respectively.



Graph 7 – Peroxide decomposition at various times

Appendix C: Raw Dat

Table 5: General information about chemicals used

Name	N-pentadecane	Squalane	Bis (4-methylbenzoyl) Peroxide	N-pentadecane Dimer
CAS-Number	529.529	111-01-3	895-85-2	-
Molar Mass (g/mole)	212.42	422.83	270.28	422.82
Density (g/cm ³)	0.769 g/cm ³	0.807	1.197	-

Table 6: Detailed calculations

	Atmosphere	N ₂	ScCO ₂								
	Temperature	130	150			130			110		
	Sample	A	A	B	C	A	B	C	A	B	C
Reaction Samples	Peroxide Weights	0.2346	0.3597	0.3601	0.3225	0.3617	0.3606	0.3604	0.3602	0.3616	0.3607
	N-pentadecane Weight	4.9985	7.69	7.69	7.69	7.69	7.69	7.69	7.69	7.69	7.69
	Total Weight of Sample	5.2331	8.0497	8.0501	8.0125	8.0517	8.0506	8.0504	8.0502	8.0516	8.0507
	Moles of Peroxide	0.000651	0.000998	0.000999	0.000895	0.001004	0.001001	0.001	0.001	0.001003	0.001001
	Theoretical Moles of Dimer	0.000651	0.000998	0.000999	0.000895	0.001004	0.001001	0.001	0.001	0.001003	0.001001
	Theoretical Mass of Dimer	0.275252	0.42203	0.422499	0.378384	0.424377	0.423986	0.422851	0.422617	0.424259	0.423203
GC-Samples	Mass Sample	1.4934	1.0455	1.0826	1.0484	1.0462	1.3036	1.0903	1.1091	1.0319	1.0576
	Mass THF	1.5007	1.039	1.0875	1.0648	1.0479	1.314	1.0891	1.1941	1.037	1.0523
	Mass Total	2.9941	2.0845	2.1701	2.1132	2.0941	2.6176	2.1794	2.3032	2.0689	2.1099

Calculations:

Moles of Peroxide:

Only 75% of the peroxide had to be taken into account since the assay provided contained 25% water. This had to be taken into account when doing calculations.

$$\text{Moles of peroxide} = \frac{0.75 * \text{Peroxide Weight}}{\text{Molar Mass of Peroxide}}$$

Moles of Dimer:

$$\text{Moles of Dimer} = \text{Moles of peroxide}$$

Mass of Dimer:

$$\text{Mass of Dimer} = \text{Moles of Dimer} * \text{Molar Mass of Dimer}$$

Appendix D: Processed Data

Table 7: Data for pentadecane experiment

	N ₂	ScCO ₂			ScCO ₂			ScCO ₂		
Temperature	130	110			130			150		
Sample	A	A	B	C	A	B	C	A	B	C
Total Area under chromatogram	2052.592	1881.106	1922.856	1874.9	2334.811	2290.269	2475.13	2492.808	2477.291	2558.208
Concentration of GC-Sample (ppm)	7848.985	7191.198	7351.341	7167.392	8931.53	8760.676	9469.768	9537.578	9478.057	9788.441
Concentration of Reaction Sample (ppm)	15736.34	14337.69	14735.96	14446.9	17877.57	17591.24	18929.11	19806.1	19002.96	19527.83
Mass of Dimer in Sample	0.08235	0.115414	0.118626	0.115756	0.143945	0.14162	0.152387	0.159443	0.153004	0.157213
Moles Dimer in Reaction Sample	0.000195	0.000273	0.000281	0.000274	0.00034	0.000335	0.00036	0.000377	0.000362	0.000372
Theoretical Mass of Dimer	0.275252	0.42203	0.422499	0.378384	0.424377	0.423086	0.422851	0.422617	0.424259	0.423203
Theoretical Moles of Dimer	0.000651	0.000998	0.000999	0.000895	0.001004	0.001001	0.001	0.001	0.001003	0.001001
Branching Efficiency	29.91795	27.34736	28.07719	30.59217	33.91913	33.47312	36.03795	37.7276	36.06385	37.14827

Calculations:

Concentration of GC-Sample:

The total area under the chromatogram was known through GC-FID. This information was used to calculate the concentration of each sample using equation (1) obtained from the calibration curve.

$$\text{Concentration of GC Sample} = \frac{\text{Total area of chromatogram} - 6.3612}{0.2607}$$

Concentration of Reaction Sample:

$$\text{Concentration of Reaction Sample} = \frac{\text{Concentration of GC Sample} * \text{Total Mass of GC Sample}}{\text{Sample Mass of GC Sample}}$$

Mass of Dimer in Reaction Sample:

$$\text{Mass of Dimer in reaction Sample} = \frac{0.001 * \text{Concentration of Reaction Sample}}{1000}$$

Moles of Dimer in Reaction Sample

$$\text{Moles of dimer in reacton sample} = \frac{\text{Mass of dimer in reaction sample}}{\text{Molar mass of dimer}}$$

Branching Efficiency:

$$\text{Branching efficiency} = \frac{\text{Moles of dimer in reaction sample}}{\text{Theoretical moles of dimer}}$$

Table 8– Branching efficiencies of various samples

	Temperature (°C)	Sample	Branching Efficiency (%)	Average Branching Efficiency (%)
ScCO ₂	110	a	27.35	28.65 ± 3.24
		b	28.02	
		c	30.59	
	130	a	33.92	34.48 ± 2.57
		b	33.47	
		c	36.04	
	150	a	37.73	36.98 ± 1.67
		b	36.06	
		c	37.15	
N ₂	130	a	29.92	-

Appendix E: Additional Squalane Experiment

Table 9: Raw Data

Peroxide mass (g)	0.3614
Squalane mass (g)	8.2825
Mass of flask (g)	47.2670
Total mass before reaction (g)	55.9209
Total mass after reaction (g)	55.7356
Net mass loss (g)	0.1853

Table 10: Processed Data

Peroxide	Molar Mass (g/mole)	270.28
	Sample Mass (g)	0.3614
	Sample Moles (mole)	0.001337
Carbon Dioxide	Molar Mass (g/mole)	44.01
	Theoretical Moles (g)	0.002674
	Theoretical Mass (mole)	0.117694
	Net Mass lost (g)	0.1853
	Degraded Product Mass (g)	0.067606